



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: **0 602 964 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **93310148.1**

(51) Int. Cl.⁵: **G11B 5/704, G11B 5/64**

(22) Date of filing: **15.12.93**

(30) Priority: **17.12.92 JP 337169/92**

(43) Date of publication of application:
22.08.94 Bulletin 94/25

(64) Designated Contracting States:
DE FR GB

(71) Applicant: **TEJIN LIMITED**
6-7, Minamihommachi 1-chome
Chuo-ku
Osaka-shi, Osaka 541 (JP)

(72) Inventor: **Hosoi, Masahiro**
8-15-15, Shakuji-machi,
Nerima-ku
Tokyo (JP)
Inventor: **Saito, Yasuhiko**
2345-8-14, Nishinabu-cho
Matsuyama-shi, Ehime-ken (JP)
Inventor: **Sasaki, Yasuhiko**
4-1-13, Kamimizo
Sagamihara-shi, Kanagawa-ken (JP)
Inventor: **Etchu, Masami**
36-30, Umegsoka, Midori-ku
Yokohama-shi, Kanagawa-ken (JP)

(74) Representative: **Votier, Sidney David et al**
CARMAELS & RANSFORD
43, Bloomsbury Square
London WC1A 2RA (GB)

(64) **Laminated polyester film for magnetic recording medium.**

(57) A laminated polyester film for a magnetic recording medium, which comprises a layer (A) of a polyester consisting essentially of a recurring unit of ethylene-2,6-naphthalenedicarboxylate and layer(s) (B) of a copolyester composed mainly of a recurring unit of ethylene-2,6-naphthalenedicarboxylate, the copolyester containing 1 to 5 % by weight of diethylene glycol component as the copolyester unit, the layer (A) being provided with the layer(s) (B) on one surface or both surfaces thereof, the laminated polyester film being biaxially oriented. Said laminated polyester is useful as a base film for a high-density magnetic recording medium.

EP 0 602 964 A1

ylate, and further contains, based on the copolyester, 1 to 5 % by weight, preferably 2 to 5 % by weight, of diethylene glycol as the copolyester unit. Further, this copolyester may contain third component(s) as the copolyester unit in a total amount of less than 1 % by weight.

5 Examples of the above third component(s) for forming the polyester and the copolyester include aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, diphenylsulfonedicarboxylic acid, 4,4'-diphenyldicarboxylic acid and benzophenonedicarboxylic acid; aliphatic dicarboxylic acids such as succinic acid, adipic acid, sebacic acid and dodecanedicarboxylic acid; alicyclic dicarboxylic acids such as hexahydroterephthalic acid and 1,3-adamantanedicarboxylic acid; 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, ethylene oxide adduct of bisphenol A, and p-xylylene glycol.

10 When the amount of diethylene glycol component or third component as the polyester or copolyester unit is calculated, glycol or diol component is defined as the residue which is formed by deleting two hydrogen atoms from two hydroxyl groups of the glycol or diol, and dicarboxylic acid component is defined as the residue which is formed by deleting two hydroxyl groups from the dicarboxylic acid.

15 The polyester forming the layer (A) and the copolyester forming the layer (B) may contain additives such as a stabilizer, a colorant and an antistatic agent. For improving the slipperiness of the film, the polyester and the copolyester may preferably contain, as lubricants, a variety of inert solid fine particles to roughen the film surface.

20 Examples of the above solid fine particles preferably include (1) silicon dioxide and its hydrate, diatomaceous earth, siliceous sand and quartz; (2) alumina; (3) silicates containing at least 30 % by weight of an SiO_2 component such as amorphous or crystalline clay minerals, aluminosilicate, calcined products thereof, hydrates thereof, chrysotile, zircon and fly ash; (4) oxides of Mg, Zn, Zr and Ti; (5) sulfides of Ca and Ba, (6) phosphates of Ni, Na and Ca, monohydrates thereof and dihydrates thereof; (7) benzoates of Li, Na and K; (8) terephthalates of Ca, Ba, Zn and Mn; (9) titanates of Mg, Ca, Ba, Zn, Cd, Pb, Sr, Mn, Fe, Co and Ni; (10) chromates of Ba and Pb; (11) carbon such as carbon black and graphite; (12) glass such as glass powders and glass beads; (13) carbonates of Ca and Mg; (14) fluorite; (15) ZnS and (16) fine particles of heat resistant polymer such as silicon resin, crosslinked acrylic resin, crosslinked polystyrene resin, crosslinked polyester resin, fluorine-containing resin and polyimide resin. Further preferred are silicon dioxide, anhydrous silicic acid, hydrous silicic acid, aluminum oxide, aluminum silicate, calcined products and hydrates thereof, monolithium phosphate, trilitium phosphate, sodium phosphate, calcium phosphate, barium sulfate, titanium oxide, 30 lithium benzoate, double salts and hydrates of these compounds, glass powders, clays such as kaolin, bentonite and terra alba, talc, diatomaceous earth and calcium carbonate. Particularly preferred are silicon dioxide, titanium oxide and calcium carbonate.

The average particle diameter of the above inert solid fine particles is preferably 0.02 to 0.6 μm , and the amount thereof is preferably 0.01 to 0.5 % by weight.

35 The polyester and the copolyester used in this invention can be produced by a method known per se.

For example, the polyester to form the layer (A) can be produced by mixing predetermined amounts of 2,6-naphthalenedicarboxylic acid and ethylene glycol, directly esterifying the resultant mixture under atmospheric pressure or elevated pressure and further subjecting the resultant esterification product to melt-polycondensation under reduced pressure.

40 The copolyester to form the layer (B) can be produced in the same manner as above except that diethylene glycol is further used in a predetermined amount. For producing the polyester or the copolyester according to the above method, a catalyst and an additive may be used as required.

The intrinsic viscosity of the polyester and the copolyester, as measured in o-chlorophenol at 25° C, is preferably 0.45 to 0.90 dl/g.

45 In the laminated polyester film of the present invention, the layer (A) of the polyester is provided with the layer (a)(B) on one surface or both surfaces of the layer (A). Therefore, the laminated polyester film of the present invention can have any one of a two-layered structure and a three-layered structure. When the laminated polyester film has a three-layered structure, the central layer is of the layer (A). The laminated polyester film is biaxially oriented.

50 In the laminated polyester film, the thickness of each layer may be determined freely, while the laminated polyester film excellently functions when the layer(s) (B) has a proper thickness. For example, when the laminated polyester film is used as a base film for a magnetic recording tape, the film thickness is preferably 3 to 12 μm and the thickness of the layer (B) is preferably at least 0.1 μm and 1/5 or less of the film thickness.

55 When the laminated polyester film is used as a base film for a magnetic recording flexible disk, the film thickness is preferably 30 to 80 μm and the thickness of the layer (B) is preferably 0.2 to 10 μm , more preferably 0.2 to 5 μm .

For using the laminated polyester film as a base film for a magnetic recording tape, the Young's moduli of the laminated polyester film both in the machine and transverse directions are preferably at least 500

(1) Young's modulus

A film was cut to prepare a sample having a width of 10 mm and a length of 150 mm, and the sample was strained with an Instron type universal tensile tester at an interchuck distance of 100 mm at a straining rate of 10 mm/minute at a chart feeding rate of 500 mm/minute to prepare a load-elongation curve. The Young's modulus was calculated on the basis of a tangent on the rising part of the load-elongation curve.

(2) Surface roughness (Ra) of film

A chart (surface roughness curve of a film) was drawn by means of a needle-contacting type surface roughness tester (Surfcoder 30C, supplied by Kosaka Laboratories) having a 2 μ m radius needle under a needle pressure of 30 mg. A portion having a measured length L in the direction of its center line is picked up from the surface roughness curve of a film. The center line of this portion picked up was regarded as an X axis, the direction of the length multiplication was regarded as a Y axis, and the roughness curve was expressed as $Y = f(x)$. The value (Ra: μ m) given by the following equation was defined as the surface roughness of the film.

$$Ra = \frac{1}{L} \int_0^L |f(x)| dx$$

(3) Heat shrinkage

A film having a length of about 30 cm and a width of 1 cm, which had been accurately measured for a length, and was placed in an oven set at 105° C under no load, and heat-treated for 60 minutes. Then, the film was taken out of the oven, allowed to cool to room temperature and measured for a difference in length between before the heat treatment and after the heat treatment. The heat shrinkage was determined on the basis of the following equation.

$$\text{Heat shrinkage (\%)} = \frac{\Delta L}{L_0} \times 100$$

wherein L_0 is a length before the heat treatment and ΔL is a difference in length.

(4) Abrasion

A film was slit to prepare a tape having a width of 1/2 inch, and the tape was allowed to run 50 m while one blade edge was vertically pressed to the tape so that the tape was pushed 1.5 mm apart from its normal running course (running tension: 60 g, running speed: 1 m/second). The abrasion was evaluated on the basis of the width of abrasion dust adhering to the one blade edge.

(5) Electromagnetic conversion characteristics

A magnetic video tape was measured for an S/N ratio with a noise meter supplied by Shibasoku K.K. Further, a difference between the above S/N ratio and the S/N ratio of a tape of Comparative Example 1 shown in Table 1 was calculated. As a VTR, EV-S700 supplied by Sony Corp. was used.

(6) Running durability of magnetic tape

While the running of a magnetic tape with a VTR (EV-S700, supplied by Sony Co. Ltd.) was started and stopped repeatedly for 100 hours, the magnetic tape was examined on its running state and measured for output. A magnetic tape which satisfied all of the following items was taken as excellent, and a magnetic tape which failed to satisfy any one of the items was taken as poor.

- (i): A tape edge did not bend and a tape did not become a wavy shape.
- (ii): A tape did not squeak in running.
- (iii): A tape underwent neither tearing nor breaking.

| | (Part by weight) |
|--|------------------|
| Acicular Fe particles | 100 |
| Vinyl chloride-vinyl acetate copolymer | 15 |
| (Eslec 7A, supplied by Sekisui Chemical Co., Ltd.) | |
| Thermoplastic polyurethane | 5 |
| Chromium oxide | 5 |
| Carbon black | 5 |
| Lecithin | 2 |
| Fatty acid ester | 1 |
| Toluene | 50 |
| Methyl ethyl ketone | 50 |
| Cyclohexanone | 50 |

The above-obtained magnetic coating composition was applied to the homopolymer surface of the above biaxially oriented polyester film so that the coating had a thickness of 3 μm . Then, the film was subjected to orientation treatment in a direct-current magnetic field at 2,500 gauss, dried under heat at 100° C, treated with a super calender (linear pressure 200 kg/cm, temperature 80° C), and taken up. The so-obtained roll was allowed to stand in an oven at 55° C for 3 days.

Further, the following back coating composition was applied to the surface (running surface) of the copolymer of the above biaxially oriented laminated polyester film so that the back coatings had a thickness of 1 μm , and dried. Further, the film was cut to prepare a tape having a width of 8 mm, whereby a magnetic tape was obtained.

Back coating composition:

| | (Part by weight) |
|---|------------------|
| Carbon black | 100 |
| Thermoplastic polyurethane | 60 |
| Isocyanate compound (Coronate L supplied by Nippon Polyurethane Industries, Ltd.) | 18 |
| Silicon oil | 0.5 |
| Methyl ethyl ketone | 250 |
| Toluene | 50 |

Table 1 shows the properties of the above-obtained film.

Examples 2 - 5 and Comparative Examples 1 - 2

Example 1 was repeated except that the amount of diethylene glycol component as the copolymer unit was changed as shown in Table 1. Table 1 shows the properties of the so-obtained films.

As shown in Table 1, the tapes obtained from the films prepared in Examples were excellent in freedom from drop-out, electromagnetic conversion, running durability and skew.

In the column of "Film structure" in Table 1, the "homopolymer" refers to ethylene-2,6-naphthalenedicarboxylate homopolymer, and the "copolymer" refers to the ethylene-2,6-naphthalenedicarboxylate copolymer having diethylene glycol (DEG) component as the copolymer unit.

Table 1 (continued)

| | Electromagnetic conversion characteristics Y-S/N (dB) | Running durability | Skew (μ .sec) | Drop-out (piece/min.) |
|-------|--|-----------------------|-----------------------|--------------------------|
| CEx.1 | -0.5 | excellent | 5 | 13 |
| Ex.1 | +0.5 | excellent | 5 | 12 |
| Ex.2 | +0.5 | excellent | 5 | 8 |
| Ex.3 | 0 | excellent | 5 | 7 |
| CEx.2 | -0.5 | excellent | 5 | 15 |
| Ex.4 | 0 | excellent | 5 | 5 |
| Ex.5 | 0 | good | 5 | 5 |

Ex. = Example, CEx. = Comparative Example

Example 6

An ethylene-2,6-naphthalenedicarboxylate homopolymer which substantially did not contain fine particles as a lubricant was prepared according to a conventional method. Further, an ethylene-2,6-naphthalenedicarboxylate copolymer having 3 % by weight of diethylene glycol component as the copolymer unit, containing 0.3 % by weight of silica fine particles having an average particle diameter of 0.1 μ m and 0.015 % by weight of calcium carbonate fine particles having an average particle diameter of 0.6 μ m, was prepared according to a conventional method. These polymers had an intrinsic viscosity of 0.65 dVg.

The above homopolymer and copolymer were separately dried and then melted in different melt-extruder, and these two polymers were allowed to come in contact in a three layer-structured extrusion die such that the homopolymer formed a central layer and that the copolymer formed two surface layers, extruded and rapidly cooled to obtain a laminated unstretched film.

The above-obtained unstretched film was stretched 3.6 times in the machine direction at 140° C, further stretched 3.7 times in the transverse direction at 150° C, and then heat-treated at 235° C for 30 seconds to give a biaxially oriented laminated polyester film having a thickness of 62 μ m.

The above biaxially oriented laminated film had a Young's modulus of 610 kg/mm² both in the machine and transverse directions, a surface layer thickness of 2 μ m each and a central layer thickness 58 μ m.

The two surface layers of the above-obtained laminated polyester film were formed of the copolymer and the void area ratio of voids formed around the silica and calcium carbonate fine particles in the surface layers was very small, as small as 1.01.

Comparativ Example 3

An ethylene-2,6-naphthalenedicarboxylate homopolymer containing 0.3 % by weight of silica fine particles having an average particle diameter of 0.1 μ m and 0.015 % by weight of calcium carbonate fine particles having an average particle diameter of 0.6 μ m was prepared according to a conventional method.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 31 0146

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|---|--|
| Category | Citation of document with indications, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. CLS) |
| X | EP-A-0 504 651 (DIAFOIL HOECHST CO) 23 September 1992 | 1-5,8,10 | G11B5/704 G11B5/64 |
| A | * page 2, line 1 - line 5 * * page 2, line 41 - page 3, line 3 * * page 3, line 25 - line 39 * * page 3, line 42 - line 57 * * page 4, line 13 - line 20 * * page 5, line 54 - line 9 * | 6,7,9,11 | |
| A | EP-A-0 510 893 (TEIJIN LIMITED) 28 October 1992 * claims 1-3 * | 1,4,8,10 | |
| | | | TECHNICAL FIELD(S) SEARCHED (Int. CLS) |
| | | | G11B |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 3 February 1994 | Examiner Klocke, S |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p> | | | |

EP 0 602 864 A1 (1994)

(19)



JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **2001347592 A**

(43) Date of publication of application: **18.12.01**

(51) Int. Cl.

B32B 9/00
B29C 55/12
B32B 27/34
B32B 27/36
C08J 7/06
C08L 67/02
/(C08L 67/02 , C08L 77:06)
B29K 67:00
B29K 77:00
B29L 7:00
B29L 9:00

(21) Application number: **2000170033**

(22) Date of filing: **07.06.00**

(71) Applicant: **UNITIKA LTD**

(72) Inventor: **KUWATA HIDEKI**
NISHITANI CHIEMI
SAKAKURA HIROSHI

(54) **GAS BARRIER POLYESTER FILM**

(57) Abstract

PROBLEM TO BE SOLVED: To provide a transparent gas barrier polyester film suitable as a packaging material excellent in gas barrier properties even under a high humidity condition and also excellent in bending resistance.

SOLUTION: The gas barrier polyester film is

obtained by forming a membrane layer comprising silicon oxide and/or aluminum oxide on at least the single surface of a biaxially stretched polyester film comprising a 60-90/40-10 (mass %) mixture of polyethylene terephthalate and polymetaxylenedipamide.

COPYRIGHT: (C)2001,JPO